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Sample Losses During Excitation

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16. ABSTRACT

Many samples of atmospheric aerosols and biological materials containing volatile or unstable species are now being examined by X-ray emission analysis, and loss of these species by sample heating is a critical consideration. The amount of heat energy deposited in a sample by the various modes of excitation may vary by orders of magnitude. For example, if one were looking for sulfur in 1-μm particles of $(NH_4)_2SO_4$, and using projectiles at typical operating energies (10-keV electrons or 3-MeV protons) as a means of excitation, about 10^3 keV of energy would be deposited per sulfur K-shell ionization produced; while photons of energy 8-keV (using Cu Kα) would deposit only about 5-keV for each K shell ionization. This paper presents calculations of energy dissipation and sample heating and loss of Al, Cu, Au, PbBrCl and $(NH_4)_2SO_4$ under typical operating conditions.

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CHAPTER 6

X-RAY EMISSION ANALYSIS: SAMPLE LOSSES DURING EXCITATION

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INTRODUCTION

Analysis by X-ray emission requires the ionization of an inner-shell electron in a sample atom. In order to produce ionization, one may use photons or charged particles for the primary exciting radiation; each of the different means of excitation has its advantages and disadvantages. Charged particles, for example, can be produced in relatively intense beams, focused and modulated in energy. On the other hand, considerably more energy must be put into a sample with charged particles than with photons to produce an X-ray. Naturally, in an analytic procedure it is desirable to change the sample as little as possible. Examination of possible effects on the sample of the energy deposition mentioned above is, therefore, important. In extreme cases, vaporization or decomposition of the sample may occur, and these problems are the subject of this paper.

In studies of elemental abundances in biological and environmental materials, increasing emphasis is being placed on the detailed distribution of elements in samples of microscopic dimension (*e.g.*, inclusions in phagocytic cells or aerosol particles collected on an air filter). When one observes these

materials by charged-particle scattering or excitation (as in a scanning electron microscope), the concentration of deposited energy in these very small sample volumes can become very high.

The energy required to induce X-ray emission resulting from photon, electron and proton excitation has been calculated and is discussed in the section below. For convenience we restrict our examples to energies in the range commonly used: 5- and 20-keV photons, 20- and 80-keV electrons, and 3- and 5-MeV protons. The K-shell ionization cross sections for these radiations in samples of Al and Cu, and the L-shell ionization cross sections in Au are given. We choose these elements because they span much of the periodic table. Energy deposited as heat in 1-μm-thick samples of these elements is reported. The relation between deposited energy and temperature is then discussed and representative calculations are reported. In the final section, we discuss the relation between temperature and decomposition or volatilization for several samples of current interest.

This paper should not be interpreted as promoting or, alternatively, criticizing a given mode of sample excitation. Our purpose is to draw information from various parts of the literature in order to make reasonable estimates of sample heating and loss and to indicate to the reader the important details that must be considered. The treatment is not rigorous; we make many approximations but have tried to indicate where they occur. We have limited our calculations to a very few representative elements and representative primary radiation energies so that the reader does not become lost in a welter of data.

IONIZATION CROSS SECTIONS AND ENERGY DEPOSITION

In the following paragraphs, we discuss energy loss and ionization cross sections for photons, electrons and protons at energies commonly used in X-ray emission analysis. The discussions of energy loss include considerations of how "local" the energy deposition is. If the primary excitation radiation transfers sufficient energy to an electron so that it leaves the sample, the kinetic energy of the departed electron will not contribute to sample heating. For this reason, the energy loss of the primary radiation may not equal the energy deposited in the sample. Since many measurements and calculations have been made of energy loss of primary radiation in numerous materials, our examination of the heating effect on small samples by these radiations will be greatly simplified if most of the energy deposited remains in the sample. On the other hand, if the sample size is such that significant loss of secondary radiation occurs, we must then know the detailed spectra of these secondary radiations in order to determine sample heating.

The energy loss processes of photons are quite different from those of charged particles. In photoionization a photon is absorbed in the sample, and a photoelectron of energy T_p is emitted; subsequently, the electron vacancy decays by emission of an Auger electron of energy T_A or an X-ray. In charged-particle ionization, a particle passes through the sample, losing energy in a series of collisions, including inner-shell ionization (the consequences of which are the same as in photoionization). In both cases, the secondary radiations—X-rays, photo-and Auger electrons, and other scattered particles—have their own characteristic energy loss processes. An enormous literature exists concerning energy loss of charged particles and photons in matter, and a good introduction to the subject is found in the text by Evans (1955).

Photons: Ionization Cross Sections

Electromagnetic radiation may interact with the sample, causing atomic or molecular excitation or photoionization, photon scattering or pair production. For the energies of interest here (1-100 keV), only photoionization is significant; and, further, most of the photoionization occurs in the shell of highest ionization potential, not exceeding the primary photon energy. The behavior can be seen in a plot of attenuation coefficients for any given element vs photon energy. The discontinuous jumps (absorption edges) in the attenuation coefficient at the successive ionization potentials show that the total photoelectric cross section is dominated by the cross section of that shell whose absorption edge lies nearest and below the energy of the exciting photon. Neglecting photoionization from less-bound shells introduces a systematic error of less than 10% (Pratt *et al.*, 1973) and permits the convenient identification of the photon attenuation cross section with the photoionization cross section of the shell of interest. It is clear that photons provide a very efficient means of exciting a sample since the most probable interaction is photoionization from the shell whose ionization potential is most nearly exceeded by the photon energy.

Our values for photoelectric cross sections come from the tables by Veigel (1973). It is, of course, important not to use a photon energy that exceeds the absorption edge of any shell more tightly bound than the one of interest. Cross sections for several representative elements and photon energies of 5 and 20 keV are given in the first two columns of Table I. For comparison with the charged-particle cross sections discussed below, the units are in 10^{-22} cm^2/atom. One can clearly see the characteristically rapid decrease in cross section with increasing photon energy by looking at the entries for Al in Table I.

Table I. Ionization Cross Sections for Photons, Electrons and Protons (10^{-22} cm^2/atom)

	Photons		Electrons		Protons	
	5 (keV)	20 (keV)	20 (keV)	80 (keV)	3 (MeV)	5 (MeV)
Al K	88	1.5	86		220	
Cu K		36	4.5	3.9	2.1	4.7
Au L		260	11	8.1	1.7	4.4

Photons: Energy Deposition

We now consider the dissipation of primary photon energy in the sample. When photoionization occurs, the ejected electron has an energy given by:

$$T_p = h\nu - \text{I.P.} \quad (1)$$

where T_p = the electron kinetic energy
$h\nu$ = the photon energy
I.P. = the ionization potential

If the dimensions of the sample exceed the range of the photoelectron, T_p will be dissipated in the sample. In Table II, we give photoelectron kinetic energies from photoionization by photons of the indicated energies in samples of Al, Cu and Au and, in μm, ranges of 10-keV electrons in these same materials. We conclude that, for sample particles of dimension $>$ 1-μm, the photoelectron energy is mostly dissipated in the sample (we neglect edge effects as a result of photoionization very near the surface of the sample). For particles around 0.1-μm or smaller, significant corrections would be necessary for reduced heating of the sample as a result of escape of the photoelectrons.[1]

Table II. Electrons Associated with Photoionization

	$h\nu$ (keV)	IP (keV)	T_p (keV)	R[a] (μm)	T_A[c] (keV)	ω[d]
Al	5	1.56	3.44	1	1.4	0.038
Cu	20	8.98	11.02	0.4	6	0.443
Au	20	11.92[b]	8.08	0.3	7.4	0.365

[a] R is the range for a 10-keV electron in the given material.
[b] For the L_3 subshell.
[c] Approximate energy for most probable transition.
Source: Bambynek *et al.*, 1972.

[1] Notice that, even for particles 1 μm on a side, one half of the mass is within 0.1 μm of the surface.

The remaining energy from the photoionization process is excitation energy associated with the inner-shell vacancy. This vacancy would, of course, also exist for alternative modes of excitation (electron, proton, etc.), and the considerations in the following paragraphs apply to them as well. The vacancy left by photoionization may decay by emission of a photon or an Auger electron. Auger electron kinetic energies (T_A) are given in Table II. A broad, often complex, spectrum of Auger electron energies will be present; we show approximate values of the most probable transitions following formation of a K vacancy in Al or Cu, or an L vacancy in Au. As with photoelectrons, comparison of the Auger electron energies with the ranges for 10-keV electrons in the given materials shows that, for samples of dimension $>$ 1 μm, losses from the sample will be small. The probability for emission of a photon (the desired event in X-ray emission analysis) rather than an Auger electron is given by the fluorescence yield:

$$\omega = \frac{\Gamma_x}{\Gamma_x + \Gamma_A} \quad (2)$$

where Γ_x and Γ_A represent the probability for photon and Auger electron emission, respectively. The entries in Table II show that only 4% of the K vacancies in Al result in K X-rays, 44% of the K vacancies in Cu result in K X-rays, and 37% of the L vacancies in Au result in L X-rays.

To summarize, ionization of inner electrons by photons is an efficient process. The vacancy created by ionization may decay by X-ray or Auger electron emission. For the elements discussed here, most of the photoelectron and Auger electron energies will be dissipated in the sample if its dimensions exceed 1 μm. Escape of photoelectrons and Auger electrons from smaller samples will reduce heating. For simplicity, we have neglected edge effects—escape of particles caused by interaction near the surface of the sample; these effects will, of course, increase with decreasing sample size. For materials not discussed here, the photoelectron and Auger electron ranges will depend on photon energy, ionization potential, Auger transition energy and sample stopping power.

Charged Particles: Ionization Cross Sections

Like photons, charged particles are most likely to dissipate their energies by ionization or excitation of atoms or molecules. The inner electron shells, however, contribute only about 10% of the charged-particle ionization cross section, and the least-bound inner shell contributes most of this 10% (Madison and Merzbacker, 1975). Thus, inner-shell ionization using charged particles is a relatively inefficient process—photons usually cause vacancies in the inner shells of interest, particles usually do not. It is for this reason

that X-ray emission analysis using charged particles rather than photons results in relatively large amounts of energy deposited in the sample per X-ray emitted.

Unlike photons, which lose their energy in a single event, charged particles lose their energy in a series of encounters with the surrounding medium. This phenomenon may complicate the determination not only of energy deposition in the sample, but also of the ionization cross sections since these cross sections depend on the primary particle energy. In Table III, we give energy losses (Pages *et al.*, 1972) for electrons and protons of the indicated energies passing through 1-μm-thick samples of the indicated materials. For protons, the energy loss is small compared to the incident energy, and we may neglect the effect of the proton energy loss on its ionization cross section. For 20-keV electrons the energy loss is not small (up to 35% of the initial energy); however, the electron ionization cross section does not depend strongly on energy in this region, and we neglect this correction.

Table III. Charged Particle Stopping Power (E) (keV/μm)

	Electrons		Protons	
	20 (keV)	80 (keV)	3 (MeV)	5 (MeV)
Al	2.6	1.0	22	16
Cu	7.2	2.8	56	40
Au	11	4.5	72	54

Experimental ionization cross sections for electrons (Powell, 1976; Davis *et al.*, 1972) and protons (Deconninck *et al.*, 1975; Hardt and Watson, 1976; Tanis and Shafroth, 1977) are taken from various sources in the literature and are given in Table I. The charged-particle ionization cross sections are not nearly so dependent on beam energy as are the photoionization cross sections. All ionization cross sections are strongly dependent on ionization potential.

Charged Particles: Energy Deposition

The energy transfer from primary radiation to its surrounding medium is the principal concern of the field of radiation dosimetry (Attix and Roesch, 1968; ICRUM, 1970) and, as already noted, the details of this transfer are especially complicated for charged particles. Moving charged particles may lose energy in inelastic collisions with electrons, interactions with nuclei, interactions with atoms or molecules as a whole, or radiative processes.

For the particles of intermediate energy considered here, only inelastic collisions with electrons are important in determining energy deposition in the sample.

Because of the requirement of conservation of momentum, the maximum possible energy transfer from the primary charged particle is restricted. For inelastic collisions with free electrons, the maximum transfer from a proton is about 1/500 of the proton energy; that from an electron is half its energy.[1] The dependence, however, of the collisions cross section or energy transfer probability on the amount of energy transferred is such that small energy transfers are greatly favored. An approximate classical expression (Evans, 1955) for the dependence of the collision cross section σ on the energy transfer Q is:

$$d\sigma = \frac{K\, dQ}{Q^2} \tag{3}$$

where K is a constant that depends on the charge and velocity of the primary projectile. Although this expression diverges as Q approaches zero, the electrons in a sample are, in fact, bound; hence, a minimum energy, greater than zero, is required for an energy transfer to take place. Using the equation above, one may calculate the mean energy transfer given the minimum and maximum energy transfer. For the energies and materials of interest here, the calculations give mean energy transfer ranging over 10-100 eV and experiments using intermediate energy electrons in thin plastic films give similar results (ICRUM, 1970). The ranges of 10-100 eV electrons in condensed matter are of the order of 10^{-3}-10^{-2} μm. Thus, we see that, although very high energy transfers from the primary charged particle to electrons in the sample are possible, most energy transfers are low; therefore, most of the energy deposition is local and we may simply use the energy loss of the primary particle as the energy deposited in the sample. Energies deposited per particle in samples 1-μm thick are taken from the literature (Pages *et al.*, 1972) expressed in units of keV/μm and given in Table III.

Figure of Merit

Our principal concern is the energy deposited in the sample. We now combine the tabulated values of ionization cross section for the various modes of excitation with the values of energy loss and extract a number that will serve as a figure of merit. For charged particles, we simply convert the

[1] Since electrons are identical, one simply defines the primary electron as that one leaving the collision with greater energy.

ionization cross sections from the units cm^2/atom to the number of ionizations N_i per particle per 1 μm of target thickness by:

$$N_i = \frac{10^{-4}\,\sigma\,\rho\,A}{M} \tag{4}$$

where ρ = the density in g/cm^3
σ = the ionization cross section from Table I
A = Avogadro's number
M = the molecular or atomic weight.

We next divide N_i by the energy lost per particle per 1 μm of target thickness from Table III to get the number of ionizations per keV energy deposited. These figures of merit for protons and electrons are given in Table IV.

Table IV. Number of Ionizations/keV of Energy Deposited in Sample

	Photons		Electrons		Protons	
	5 (keV)	20 (keV)	20 (keV)	80 (keV)	3 (MeV)	5 (MeV)
Al K	0.29		2.0×10^{-2}		5.9×10^{-3}	
Cu K		9.1×10^{-2}	5.3×10^{-4}	1.2×10^{-3}	3.2×10^{-5}	1.0×10^{-4}
Au L		0.12	5.9×10^{-4}	1.1×10^{-3}	1.4×10^{-5}	4.8×10^{-5}

Since photons are so efficient in photoionization, we may simply approximate the energy deposited per ionization as the photoelectron kinetic energy; thus the number of ionizations per keV of energy deposited is just the reciprocal of that number taken from Table II. The photon figures of merit also are given in Table IV. In order to calculate the number of X-rays emitted per keV of energy deposited, one must take the fluorescence yield and Auger electron energies into account for both photon-and charged-particle-induced X-ray emission.

A comparison of the figures of merit in Table IV shows that photons are the most efficient means of producing inner-shell ionizations in thin samples; electrons are next in efficiency, and protons are last. We emphasize that this comparison is a very limited one. We have not answered the broader (and more directly related to an analytical experiment) question of the minimum amount of material that can be detected at some confidence level for a given energy input. The answer to the broader question depends also on the background generated by the various excitation modes. For example, although electrons are more efficient than protons in producing ionizations for a given amount of energy deposited in the sample, an electron beam generates considerably higher amounts of bremsstrahlung radiation than does a proton beam. For the particle energies used here, proton-induced X-ray analysis is more sensitive than electron-induced X-ray analysis. Detailed considerations of this sort are beyond the scope of this paper.

DEPOSITED ENERGY AND SAMPLE TEMPERATURE

We now consider the relation between energy deposition in a sample and the resulting sample temperature. A beam of charged particles of current I (A) which uniformly illuminates the sample for τ seconds and loses E (keV) per particle in the sample will deposit Q calories according to:

$$Q = 239\ I\,E\,\tau \quad \text{cal} \tag{5}$$

If we have a particle of volume V (cm^3), heat capacity C (cal/deg gram), and density ρ (g/cm^3), heated by Q calories and *do not allow for heat loss* by radiation or conduction, the temperature will rise by ΔT (deg) according to:

$$\Delta T = \frac{Q}{C\,\rho\,V} \quad \text{deg} \tag{6}$$

We neglect the temperature dependence of C here and in subsequent calculations; it may become significant at high temperatures.[1]

It turns out that the product ($C\rho$) for many solid materials (elements, minerals, inorganic and organic compounds) ranges from 0.4-0.8 cal/deg cm^3; this means that many particles of different composition but the same size have roughly the same heat capacity. We calculate ΔT for a particle with V = 1 μm^3 and $C\rho$ = 0.6 cal/deg cm^3. The result is:

$$\Delta T = 4.0 \times 10^{14}\ I\,E\,\tau \quad \text{deg} \tag{7}$$

In order to appreciate the magnitude of possible sample heating, we use these and subsequent general equations to calculate heating resulting from electron beams for a very limited set of experimental circumstances. From Table III, we see that typical electron energy losses E in 1-μm-thick samples are of the order of 2 keV. Using E = 2 keV, we find that to keep the temperature rise below 1000°C *for a particle that does not radiate or conduct*, we are restricted to:

$$I\tau < 10^{-12} \text{ A sec} \tag{8}$$

[1] Assuming C is constant neglects the temperature dependence of C (often expressed as $C = a + bT + cT^{-2}$) and possible phase changes. The temperature dependence of C may become important at high temperatures. A phase change will interrupt the heating of a pure sample until it is complete and may significanlty increase the time required for a sample to reach a given temperature. If the enthalpy of the phase change is known, the time for a sample of given mass and heated by a given current to pass through the change can be calculated (see section entitled "Heating of PbBrCl and $(NH_4)_2SO_4$").

The sample does, of course, lose heat by radiation and conduction once it exceeds the temperature of its surroundings. The radiative heat loss Q_R is a function of the difference in temperature between the sample T and its surroundings T_s and is given by the Stefan-Boltzmann Law:

$$Q_R = K \epsilon a \tau (T^4 - T_s^4) \quad \text{cal} \tag{9}$$

where ϵ = the emissivity of the sample (maximum = 1)
a = the area of the emitting surface
K = the Stefan-Boltzmann constant

We define an equilibrium temperature T_e such that at T_e the energy absorbed by beam heating and energy emitted by radiation are equal. Note that because of the very strong dependence of Q_R on T, T_e will be rather insensitive to small changes in ϵ and a and even in Q_R itself.

We may now calculate T_e for the hypothetical particle from the previous example, assigning to it an emissivity of 0.5 and an emitting area equal to that of a cube of volume 1 μm^3; the temperature of the surroundings is 300°K. The values of T_e for a range of beam currents I are given in Table V.

Table V. Beam Heating of a 1-μm^3 Sample

I (A)	T_e (°K)	τ 80% (sec)
10^{-14}	301°	
10^{-12}	375°	0.13 (360°K)
10^{-11}	595°	0.041 (536°K)
10^{-10}	1042°	0.0092 (894°K)
10^{-9}	1851°	0.0018 (1540°K)
10^{-8}	3291°	0.00038 (2690°K)

Note: $\epsilon = 0.5$; $a = 6 \times 10^{-8} cm^2$; E = 2 keV; $T_s = 300°K$; $C\rho = 0.6$ cal/deg cm^3

The relation between time τ and temperature T is obtained by solving the differential equation for energy into and out of the sample:

$$Q = C\rho V \frac{dT}{d\tau} + K \epsilon a (T^4 - T_s^4) \quad \text{cal/sec} \tag{10}$$

where Q is the number of calories per second deposited in the sample by the beam and the remaining symbols have already been defined. The solution for the above equation for constant Q is:

$$\tau = \frac{1}{2rs^3}\left[\frac{1}{2}\left\{\ln\frac{1+(r/s)T}{1-(r/s)T} - \ln\frac{1+(r/s)T_s}{1-(r/s)T_s}\right\} + \mathrm{Tan}^{-1}(r/s)T - \mathrm{Tan}^{-1}(r/s)T_s\right] \quad \text{sec} \tag{11}$$

where $r = (K \epsilon a / C \rho V)^{1/4}$ deg$^{-3/4}$ sec$^{-1/4}$

$s = [(Q + K \epsilon a T_s^4)/C \rho V]^{1/4}$ deg$^{1/4}$ sec$^{-1/4}$

The behavior of this expression is such that the equilibrium temperature is approached asymptotically. Using this equation, we calculate the time ($\tau_{80\%}$) for 80% of the temperature rise from T_s to T_e, and these values are found in the third column of Table V. The temperatures reached in that time are given in parentheses.

As shown in Table V, the temperature reached by the sample and the time for sample heating are extremely sensitive to the current. These results are rather general, given the beam current and beam spot size; as we have already noted, the heat capacity and emissivity used are representative of a large range of materials. The other variables are sample volume and area. The treatment here is approximate in that we have assumed uniform heating of the sample. We have neglected heat losses by conduction—this depends critically on the detailed properties of the sample and sample support, and a general analysis does not appear to be feasible. If the particle has a significant area of physical contact with a substrate of high conductivity, the beam heating effects discussed in this paper will be diminished. The calculations presented here would apply, for example, to analyses of irregularly shaped particles in poor contact with the substrate or on a substrate with poor conductivity.

We emphasize again that different experimental arrangements may change sample heating effects enormously. Electron excitation experiments are often done in a scanning mode: the beam sweeps across the sample and may not spend sufficient time on a given area to cause damage before moving on and allowing the sample to cool (Nickel *et al.*, 1976). Proton beams are not often scanned; however they are typically used in the analysis of macroscopic samples. In this type of application, the beam areas are of the order of 1 cm^2 and, consequently, sample heating is diminished.

MATERIALS AT HIGH TEMPERATURES

Given the free energies of the materials of interest and their vapor phases and various possible decomposition products, we may calculate the equilibria for vaporization and/or decomposition (Lewis and Randell, 1961). Although most X-ray emission experiments are not carried out under equilibrium conditions, these calculations will indicate at what temperatures significant

loss of sample by vaporization and decomposition will begin to occur. Throughout, we neglect loss of heat from the sample by conduction.

Lead Dichlorides and Dibromides

Here we consider the sample losses for $PbBr_2$ and $PbCl_2$ compounds, which are chemically and physically similar to the mixed PbBrCl compounds found in automobile exhaust (Stull *et al.*, 1970). The lead dihalides are stable to decomposition well above their boiling points; hence, losses of these materials as a result of heating would occur by vaporization. The vapor pressures of $PbCl_2$ and $PbBr_2$ are 10^{-2} atm at 908 and 870°K, respectively, and 1 atm at 1227 and 1187°K, respectively. We conclude that losses of the lead halides by volatilization will become significant at about 900°K.

Ammonium Sulfate

Although ammonium sulfate is stable at room temperature, its products of decomposition (NH_3, SO_3, H_2O) are all gases above 373°K; hence, we expect the stability to be strongly dependent on temperature. In fact, it has been shown (Erdey *et al.*, 1964) that significant decomposition:

$$(NH_4)_2\,SO_4\,(c) \rightarrow NH_4\,HSO_4\,(\ell) + NH_3\,(g)$$

occurs above 500°K. The decomposition:

$$NH_4\,HSO_4\,(\ell) \rightarrow H_2SO_4\,(g) + NH_3\,(g)$$

occurs above 620°K. It was observed in these experiments that the decomposition products were very active and would fuse various metal oxides (Erdey *et al.*, 1964). At these temperatures, the H_2SO_4 is largely dissociated into SO_3 and H_2O (Stull *et al.*, 1970). We conclude that losses of $(NH_4)_2SO_4$ as a result of sample heating will become significant when the sample temperature exceeds 500°K. Because of the activity of the decomposition products SO_3 and H_2SO_4, sulfates may be formed by reaction with other materials in the vicinity.

Heating of PbBrCl and $(NH_4)_2SO_4$

As discussed previously, we may calculate the time-temperature relationships including heat losses by radiation for a sample exposed to a beam of electrons. The calculations require that we know or estimate the sample heat capacity, density and emissivity; the energy deposited per electron in the sample; and the beam current. These values are given in the first five columns in Table VI for $(NH_4)_2SO_4$ and PbBrCl[1] for 10^{-10} ampere beams

[1]The properties of PbBrCl are estimated from those of $PbBr_2$ and $PbCl_2$.

Table VI. Sample Properties, Decomposition Temperatures and Times

	C (cal/gm deg)	ρ (g/cm^3)	ϵ	E (keV/μm)	I (A)	T_D (°K)	τ_D (msec)
$(NH_4)_2SO_4$	0.34	1.77	0.5	3[a]	10^{-10}	500	0.2
PbBrCl (s)	0.062	6.3	0.5	2.2[b]	10^{-10}	900	8
PbBrCl (ℓ)	0.082	6.3	0.5	2.2[b]	10^{-10}	900	8

of 20-keV electrons on $(NH_4)_2SO_4$ and 80-keV electrons on PbBrCl. The sixth column gives the temperatures T_D at which sample loss occurs as discussed above. The last column gives the time τ_D required for a 1-μm particle, uniformly heated by the beam, to reach T_D from an original temperature of 300°K. For $(NH_4)_2SO_4$, the time is 0.2 msec. The sample loss temperature of PbBrCl is above the melting point, and hence we must calculate the time for a solid sample to be heated from 300°K to the melting point, the time for melting, and the time for the liquid sample to reach the decomposition temperature. These times are 3, 2 and 3 msec, respectively.

CONCLUSIONS

This work has outlined the necessary considerations in determining sample heating by beams of photons or charged particles, and we summarize our conclusions:

1. Photons are considerably more efficient in creating inner-shell ionizations than are charged particles.
2. One can easily determine energies deposited in samples 1 μm or larger by photons or charged particles. For particles smaller than 0.1 μm, significant surface losses may occur and the detailed energy spectra of secondary radiations must be known.
3. Neglecting conduction losses, one can easily calculate the equilibrium temperature of a heated particle. Because of the T^4 dependence of the radiated heat, small errors in sample area, emissivity, or heat input are negligible—a combined error of a factor of two in these values leads to an equilibrium temperature difference of 20%.
4. The use of small charged-particle currents in an examination of small particles can cause very rapid rises in sample temperature leading to loss by decomposition or volatilization.

Each excitation mode has its own advantages; for example, photons deposit considerably less heat in irradiated samples than charged particles do. Charged particles, however, may be focused and used as microprobes to examine elemental distributions in microscopic samples. Although protons deposit more energy in samples than electrons do, they generate less

background radiation and are not scattered so strongly as electrons. The weaker scattering of protons permits them to be brought through a thin window without large resolution losses, permitting examination of samples at atmospheric pressure. These and many other characteristics of photons and charged particles illustrate the important role each has in X-ray emission analysis. In these experiments, however, it is often critically important to determine the effects of sample heating.

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8